Self-organizing Molecular Semiconductors: Synthesis, Properties, and Applications

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Duration : April, 2001 – March, 2004

Abstract

The SOMS team has studied synthesis, properties and their physical basis, and applications of discotic and smectic liquid crystals with insight into their future development as a self-organizing molecular semiconductor (SOMS). The goal of the present research is to establish a firm basis for their future applications to the opto-electronic devices. As a result, we established the advanced basis to clarify their general features of properties and re-confirmed their high potential for a new type of quality organic semiconductors on the experimental basis of synthesizing new SOMS with excellent charge transport properties, establishing the physical basis in understanding their unique properties of charge carrier transport, and fabricating a proto-type of devices.

Keywords: Discotic liquid crystal, Smectic liquid crystal, Organic semiconductor, Charge transport, Mobility

1. Introduction

In 1990s, it was found that some types of liquid crystals exhibited fast electronic conduction that was 100 ~ 1000 times faster than that of conventional amorphous organic semiconductors by Haarer and Hanna of the present research team members. This discovery gave the liquid crystal a new aspect of “self-organizing molecular semiconductor” (SOMS). The purpose of the present research project is to establish a firm basis for the device application of the SOMS in the future, through a collaborative research on its synthesis, properties, and applications. The team was started with 5 principal members from Japan, Germany, the United Kingdom, and the United States, and was joined by a new member of Prof. Dunlap in the second year for enhancing the research activity in the theoretical understanding of charge carrier transport in the SOMS. We expected to give the answers to the following questions about the SOMS after this three years collaborative research:
1. What are the most important factors that influence charge mobility in SOMS?
2. How can the carrier transport in SOMS be understood theoretically?
3. What are the theoretical or practical limits of charge mobility in SOMS?
4. How can SOMS be designed with both high mobility and other important ancillary properties?
5. How can the carrier injection at the interface with the electrode materials be controlled and optimized?
6. What are the most unique phenomena and device structures involving SOMS?
7. What are the most promising technological applications for exploitation of SOMS?

We held a special symposium for the SOMS every year for stimulating the research activity in related communities, in addition to for discussing research results of the year, and promoting a new advance of the collaborative research: the special symposium in the Annual Spring Meeting of Japanese Society of Applied Physics, titled by Towards a New Horizon in Organic Semiconductors (March 2002, Hiratsuka, Japan); Joint Symposium on Organic Photonic Materials and Devices V, in Photonic West sponsored by SPIE (January 2003, San Jose USA); a Special Symposium in Materials Congress 2004 sponsored by Royal Society, titled “Self-organized Liquid Crystal Semiconductors” (March 2004, London, UK).

2. Results and Discussion

2.1. Synthesis of new SOMS materials

It is not the time to give an exact answer to the following questions yet, “What are the most important factors that influence charge mobility in SOMS?” and “How can SOMS be designed with both high mobility and other important ancillary properties?” because of insufficient systematic synthesis of the new SOMS materials and their characterization. But, it is pointed out that the mobility is determined by an intermolecular distance of the molecules in the mesophase, and that the large π-conjugate system in the core moiety is favorable for high mobility, judging from the accumulated results on the molecular structures, mesophase behaviors, X-ray diffraction data, and characterization of charge carrier transport properties of the materials synthesized. Since the molecular structures of the SOMS is rather simple, we think that it is possible to show the guiding principle for materials design of the SOMS with a high mobility and a good compatibility to the device applications, when those data are accumulated enough. In fact, the mobility of the discotic SOMS is challenged to explain by calculation of transfer integral of the molecular orbitals in the two oriented molecules, based on the first principle. For this achievement, we need further investigation based on both experimental and theoretical approaches.

In this project, Leeds University studied new discotic materials for SOMS including Triphenylenes and their block polymers and Phthalocyanines, and Tokyo tech and Kent State University did calamitic materials including 2-Phenyl-naphthalenes, 2-Phenylbenzothiazole, Biphenyls, Terphenyls, Terthiophenes, Quaterthiophenes, Phenylpyridines, and Polyacrylate containing Phenynaphthalene-moiety as a mesogenic group, in addition to a polymer composite prepared with 2-phenynaphthalene derivative and cross-linker. All the materials synthesized were purified by column chromatography and/or recrystallization for characterization of charge carrier transport.
properties. The followings are our new findings of the three years research.

(1) High mobility at ambient temperatures and up to 0.1 cm²/Vs

Leeds group discovered that some large-size discotic materials formed a new discotic columnar phase with a triphenylene derivative under complementary polytropic interaction (CPI), and synthesized the CPI-discotics extensively. It was found that the CPI discotics exhibited higher mobility by 2 to 3 orders of magnitude compared with its components of a CPI pair, and the highest mobility was over 10⁻² cm²/Vs. In addition, Leeds group achieved the highest hole mobility of 0.2 cm²/Vs characterized by TOF measurement in the columnar phase of 1,4,8,11,15,18,22,25-Octaactylophthalocyanine, which exhibited homeotropic alignment easily.

In smectic liquid crystals, Tokyo Tech group found that the high mobility over 10⁻² cm²/Vs was achieved in the highly ordered SmE, SmBₜₚ, SmG phases of 2-Phenylnaphthalens, Terthiophens, Terphenyls, and Quaterthiophenes. Above all, some derivatives of 2-Phenylnaphthalene, Terthiophene, and Quaterthiophene exhibited the high mobility over 10⁻² cm²/Vs at ambient temperatures. In addition, the highest mobility over 0.1 cm²/Vs was achieved in the smectic liquid crystals of Quaterthiophene derivative. In general, the smectic SOMS has a small core moiety compared with the discotics, and are easy to synthesize. Therefore, this compatible mobility of 0.1 cm²/Vs to the highest mobility in discotics is very favorable for device applications.

(2) SOMS with a wide temperature range for a mesophase

It is necessary for SOMS to have a wide temperature range of a mesophase with a high mobility, e.g., -20 ~ 80 °C for device applications. For extending and reducing the mesophase temperature, the blend technique with different liquid crystals is available, and is utilized generally in display applications. However, it is not always the case for SOMS because of the limitation of available SOMS to mix without deterioration of the charge carrier transport properties. Therefore, demonstrating a fact that there exists a high mobility SOMS with a wide temperature range for a mesophase is important in the early stage of the research. In fact, it was demonstrated that some of 2-phenylnaphthalene, Terthiophene, and Terphenyl derivatives showed a high mobility over 10⁻² cm²/Vs at the wide temperature range of -20 ~ 80°C.

(3) Polymeric SOMS

Polymeric SOMS is a good candidate for immediate applications and for plastic electronics. In fact, poly-9,9-dialkylfluorenes that are π-conjugated main chain polymers exhibit a high mobility up to 8 × 10⁻³ cm²/Vs in nematic phase. However, several trials to realize a high mobility in polymeric SOMS with discotic core moiety have not been successful so far because of the disordered molecular alignment in the polymers. Thus, an acrylate polymer having 2-phenylnaphthalene moiety in the side chain was synthesized to explore the fast charge carrier transport in its mesophases. And it was found that the acrylate in the SmA phase at higher temperature over 110°C exhibited a comparable mobility of 10⁻⁴ cm²/Vs to that of SmA phase in small molecular weight liquid crystals with the same core moiety, and that the smectic glassy phase at room temperature exhibited a high mobility of 10⁻³ cm²/Vs when mixed with a small amount of the small molecular weight liquid crystal. This result is
important as the first experimental evidence that the polymeric smectic SOMS exhibits the mobility as high as those of the small molecular weight SOMS.

(4) SOMS polymer gel

The polymeric SOMS is beneficial for fixing the molecular alignment in the mesophase and easy fabrication of thin films. Thus, it was established a new composite of polymer and SOMS by photopolymerization of a cross-linker: the charge carrier mobility of the resulting composite consisting of cross-linker up to 20wt% was not degraded when polymerized in mesophases, while it was very much degraded when polymerized in isotropic temperature. Furthermore, the polymer content (cross-linker) content was increased up to 50% when the chemical structure of the cross-linker was appropriately selected.

2.2 Characterization of electrical properties in SOMS

The charge carrier transport properties of the SOMS newly synthesized were characterized by TOF experiments and the following new findings were revealed.

(1) Electronic and ionic conduction in SOMS

From the characterization of the charge carrier transport in purified and intentionally doped SOMS, it was revealed that there co-existed two different conduction mechanisms in SOMS, i.e., electronic and ionic conduction. This can be possible due to the different charge carrier pathways in SOMS: because of the inhomogeneous mesophase structure consisting of the flexible hydrocarbon and a well aligned p-conjugated core moiety in SOMS, the electronic conduction takes place in the core region and the ionic on in the hydrocarbon region. In fact, it was confirmed experimentally that the contamination of chemical impurities causes a shift of conduction mechanism from electronic one to ionic one, which does not depend on whether the impurities are ionic or non-ionic, but where their HOMO or LUMO levels is in terms of those of SOMS. This indicates strongly that the SOMS for device applications must have a high purity and that it is quite important to develop a purification technique for SOMS.

(2) Bipolar charge carrier transport

In disotic SOMS, it has been revealed that the negative charge carrier exhibited a low mobility on the order of $10^{-5}$ cm$^2$/Vs compared with hole mobility over $10^{-3}$ cm$^2$/Vs by one of this team member, Prof. Haarer, while both electron and hole have almost same mobility over $10^{-3}$ cm$^2$/Vs in smectic SOMS. According to the recent understanding in the charge carrier transport in smectic SOMS, it was suspected that the slow negative charge carrier transport in the triphenylenes was attributed to the ionic conduction resulting from contamination of impurities. Thus, the negative charge carrier transport in H4T and H5T was re-investigated, and it was found that the electron transport took place in purified H4T and H5T, and their mobilities were comparable to those for holes, i.e., $10^{-3}$ cm$^2$/Vs and $10^{-2}$ cm$^2$/Vs, respectively. This new findings disclosed a general feature of charge carrier transport in SOMS.
(3) Poole-Frenkel-like behavior of the mobility at low temperature region

One of the unique features of charge carrier transport in SOMS is temperature- and electric field-independent mobility in mesophases, which can be understood by a hopping transport model in a narrowly distributed density of states in SOMS as described later on. This model predicts the Poole-Frenkel-like behavior of the mobility at a low temperature region. This was confirmed experimentally by the characterization of charge carrier transport properties in a Terthiophene derivative and its mixture that exhibited a wide mesophase temperature range below 0°C, which was a good support for the present charge transport model proposed for SOMS.

(4) Characterization of Photoconductivity

The photoconductivity in a model compound of smectic SOMS, i.e., 2-phenylnaphthalene derivative, was characterized: the $\mu \tau$-product was estimated to be $3 \times 10^{-7}$ cm$^2$/V and $6 \times 10^{-8}$ cm$^2$/V in SmA and SmB phases, respectively, where the TOF collected charge measurements were carried out at different electric field in taking account of field dependence of charge generation. In addition, the charge carrier lifetime was also determined by TOF experiments with the purified model compound to be $\approx 10^{-2}$s and $10^{-5}$s for holes and electrons, respectively, the latter was determined by trapping at the deep states attributed to chemical impurities.

The photo-charge generation process was investigated in H6T of a triphenylene derivative and found to be governed by a dissociation of excitons photo-generated in the H6T at the electrode interface.

2.3 Exploration of new functionalities in SOMS

The SOMS is a new type of organic semiconductors exhibiting liquid crystallinity and fast charge carrier transport enhanced by self-organized molecular alignment. In fact, totally new applications could be available if any new functionality was disclosed in addition to the unique semiconducting properties. In this project, however, the exploration of the new functionalities has not been carried out fully because of the limited time. The following new results were established to answer the questions partly, “How can the carrier injection at the interface with the electrode materials be controlled and optimized?” and “What are the most unique phenomena and device structures involving SOMS?”

(1) Electrical properties at the interface between SOMS and electrode materials

The electrical properties at the interface between SOMS and electrode materials have not been clarified yet because of the relatively new discovery of the SOMS, while those at the interface between the solid organic semiconductor and electrode materials is fairly well understood. Thus, they were investigated with a model system of a 2-phenynaphthalene derivative of smectic SOMS and metal electrodes. It was found that there were two different regimes in the charge injection from the electrodes according to the electric field applied: at the range over $10^5$V/cm, the current was dominated by the charge injection from the electrode, which followed Schottky–type injection regime; the energy barrier of 1.5–2.0eV, however, was not determined simply by the energy difference between the Fermi level of the electrode materials and HOMO level of the SOMS; it had to be
taken account of the vacuum level shift just as in the case of the solid organic semiconductors; at the range below \(10^5\) V/cm, the current was proportional to the electric field, where its activation energy was constant to be 0.8–0.9eV irrespective the field, indicating a different charge injection mechanism.

(2) Enhanced charge injection induced by bias annealing

It was found that the current injection was drastically enhanced at the triphenylene/electrode interface by 6 orders of magnitude, when the cell was annealed at the isotropic phase under applied electric field. This phenomenon was explained by formation of electrically double layers due to the accumulation of ionic species during bias annealing, which enhanced charge injection at the interface.

(3) Spectral sensitization of Soms

The spectral sensitization of photoconductivity in a triphenylene derivative was investigated with C\(_{70}\), and it was found interestingly that both electron and hole currents were enhanced and the mobility was not deteriorated by addition of C\(_{70}\) into the triphenylene even at a high concentration of 1 %. This phenomenon can be probably explained by the segregation of C\(_{70}\) at the vicinity of the electrode surface, which was induced by microphase separation. This is a very characteristic behavior in the mesophase materials that have inhomogeneous structures aggregating in columns or layers.

2.4 Understanding of charge carrier transport properties

As described above, the charge carrier transport in the SOMS is very unique and different from that of organic amorphous materials. Therefore, to understand what governs the carrier transport in the SOMS is very important for us to recognize the scope and limitation of the charge carrier transport properties of SOMS. With modeling of charge carrier transport in the smectic SOMS and its computer-aided simulation, in addition to theoretical analysis of the transient photocurrent of 2-phenylnaphthalene derivative, it was clarified that the characteristic charge carrier transport in the SOMS was able to well describe in the framework of the hopping transport in narrowly distributed density of states. This also gives an answer to the question, “What are the theoretical or practical limits of charge mobility in SOMS?”. According to the present understanding about the charge carrier transport in SOMS, the theoretical upper limit of the mobility in SOMS is considered to be 1 cm\(^2\)/Vs where conduction mechanism is decided to be band-like or hopping. Taking account of the electrically inactive domain boundaries in the SOMS, the practical upper limit of the mobility in SOMS is estimated to be 1 cm\(^2\)/Vs also. This is comparable to the mobility in the organic polycrystals. This conclusion encourages us to go on further for device applications of SOMS.

(1) Theoretical understanding of charge carrier transport in SOMS

It has been revealed in various liquid crystals as described in the section 2 that the electronic conduction in the SOMS was quite different from that in amorphous organic semiconductors, since it was discovered in triphenylene and 2-phenylbenzothiazole derivatives: the charge carrier mobility depends on neither electric field
nor temperature. By characterizing the charge carrier transport in the biphenyls synthesized, it was found that the Poole-Frenkel type behavior was observed in SmE phase while the mobility did not depend on electric field in SmB phase. On the basis of this finding, we modeled the charge carrier transport in smectic SOMS as the 2-dimensional hopping transport in the distributed density of states, and analyzed its charge transport characteristics of a model material, i.e., a 2-phenylnaphthalene derivative, by Monte-Carlo simulation. This revealed that the charge carrier transport in the 2-phenylnaphthalene derivatives could be explained by the 2-dimensional hopping transport in narrowly Gaussian-distributed density of states of 60meV.

Furthermore, the analysis of localized density of states in the model material was carried out by the curve fitting of transient photocurrent with a charge transport equation based on the multiple-trapping model, and it directly revealed a shape of the trap states to be Gaussian with a narrow width of 50meV. Thus, all the results analyzed were consistent with the model described above. This model also explains that the charge carrier transport is not affected by electric field and temperature as a result of thermalization of carriers with $kT$ in spite of trap states or distributed density of states. In fact, the density of states was determined to be Gaussian with a narrow width of 40~50meV in smectic SOMS as described in the section 2.

On the other hand, in the discotic SOMS, the carrier transport was explained by 1-dimensional hopping transport in distributed density of states. Recently, in a new approach based on a theoretical calculation of transfer integral of a pair of triphenylene molecules, the mobility has been estimated as a function of molecular configuration of the molecules in Derft University group with the collaboration of team member. This new approach will open up a new insight into the charge carrier transport in discotic SOMS. Furthermore, as for the new approach to understand the charge carrier transport, “Random phase or Granular Disorder model” and ”the space charge effect in low-dimensional system” were discussed also according to results obtained by Monte-Carlo simulation of the model system.

2.5 Applications of SOMS

According to the accumulated results on the charge carrier transport in the SOMS, the SOMS is very advantageous over the amorphous materials for device application in terms of high quality organic semiconductors. However, for the original devices with the SOMS, the exploration of new functionality in the SOMS has not been done enough yet. Therefore, we have had no definite answer for the question, i.e., “What are the most unique phenomena and device structures involving SOMS?” and “What are the most promising technological applications for exploitation of SOMS?” The followings are something interested.

(1) Inter-chip connect with SOMS

A demonstrator for two chip and three chip stacks in which the inter-chip conducting elements are homeotropically aligned discotic liquid crystal was fabricated successfully, where the through-chip conducting elements were electrodeposited copper in small bias. Connecting pads on the surface of each chip were of the order of 2mm square. This work has stimulated commercial interest and further funding.
(2) Polarized light emitting diodes \(^{(18)}\)

The electroluminescence device was fabricated with a 2 \(\mu\text{m}\) thick liquid crystal cell having ITO electrodes, which was capillary-filled with a terthiophene derivative of \(\omega, \omega'-\text{dihexyl} \text{terthiophene} (6\text{-TTP-6})\). The EL cell emitted green polarized light at the brightness of 50cd/m\(^2\) when biased at 50V, whose dichroic ratio was over 10.

(3) Photoreceptors for electrophotography \(^{(19)}\)

The electrophotographic photoreceptor was fabricated by covering the surface of a 100 \(\mu\text{m}\) thick layer of a 2-phenylnapthtalene derivative of 8-PNP-O12 on a conductive substrate with a 12 \(\mu\text{m}\) thick thin polyester film. The basic performance was characterized to demonstrate its feasibility of image formation by photo-induced discharge technique and image formation with the toner development. The first toner image was obtained by the SOMS photoreceptor.

(4) TFT application \(^{(20)}\)

The bottom gate thin film transistor (TFT) was fabricated with a vacuum-evaporated 50nm thick quaterthiophene film of \(\omega, \omega'-\text{dioctylquaterthiophene}\) on SiO\(_2\)/Si-wafer (8-QTP-8), whose channel width and length were 1200 and 50 \(\mu\text{m}\), respectively. The resulting TFT exhibited a p-channel performance of \(V_{\text{th}}=10\text{V}, \text{On/Off ratio}=10^4\), and \(\mu_{\text{FET}}=0.001\text{cm}^2/\text{Vs}\).

3. Conclusion

Under the international collaboration with 6 SOMS team members in Japan, Germany, United States, and United Kingdom, we have studied “Self-organizing Molecular Semiconductor, SOMS”, i.e., discotic and smectic liquid crystals, with respect to their materials synthesis, properties, and applications for three years in order to establish the scientific and technological basis for their device application in the future.

As for the materials synthesis, we haven’t come to a full conclusion that gives us a guiding principle for molecular design of the SOMS suitable for device applications yet. However, we could indicate the basic requirement for as for the SOMS exhibiting the high mobility and/or a wide mesophase temperature range. In fact, we could obtain the highest mobility of 0.2 and 0.1 cm\(^2/\text{Vs}\) for the discotic and smectic SOMS, respectively, which were determined by time-of-flight measurement for the first time. Furthermore, we could prepare the SOMS exhibiting a wide mesophase temperature range from –20\(^\circ\text{C}\) to 80\(^\circ\text{C}\), and even at –100\(^\circ\text{C}\). These can be a good basis in the materials design for preparing the practical materials suitable for device applications.

In the characterization of charge carrier transport in SOMS including newly synthesized SOMS, we confirmed that the bipolar charge carrier transport took place in both ionic and electronic manners basically, and the electronic mobility depended on neither temperature nor electric field at the mesophase temperatures over the room temperature range. In addition, the electrical properties at the interface of electrode materials and SOMS were clarified for the first time and could be a good basis for device-oriented studies.

As the results of efforts to understand the unique charge transport characteristics in the SOMS, we could propose a model for explaining them, i.e., a 2-dimensional hopping transport in the Gaussian-distributed density
of states with a narrow width of ~50meV, based on the theoretical analysis of the charge carrier transport by a new method based on the multiple trapping model and the Monte Carlo simulation of a model system. The model could explain the Poole-Frenckel-like behavior of the charge carrier transport in SOMS at a low-temperature region below room temperature, which was clarified in the SOMS exhibiting mesophase at low temperatures. This model provides us with a theoretical scope and limitation for the charge carrier transport in SOMS: we indicate the upper limit of the mobility in SOMS to be 0.1~1 cm²/Vs, which is expected to be same as the mobility in a polydomain texture of SOMS because of electrically inactive domain boundaries.

In applications of SOMS, new applications such as an inter-chip connect material for LSI technologies, organic thin film transistors, and polarized electroluminescence devices were proposed and demonstrated by fabricating the prototype devices, in addition to the applications as a high quality organic semiconductor for conventional device applications such as Xerographic photoreceptors and photosensors.

With the various experimental results described above, now we can describe the high potential of SOMS, i.e., self-organizing molecular semiconductors as a quality organic semiconductor more clearly. According to the accumulated results from these three years collaborative research, we can give the answers up to 70 % to the questions as described in the first section.

In summary, we conclude that the SOMS is very promising for the organic opto-electronic devices in the future.

4. Future scope

Through our three years collaborative study, we have demonstrated how the SOMS are promising as a new organic semiconductor over the organic amorphous semiconductors and compatible to the organic polycrystalline semiconductors. For the device applications in the future, however, we need to study more about the materials design for the practical materials and to explore new devices with SOMS, in addition to establishing the processes technologies for making the best use of the unique nature of SOMS. We, the members of the SOMS team, do expect that the SOMS research is promoted for the practical applications by the researchers who find interests in SOMS with the present results.

5. Acknowledgement

All the SOMS team members, JH, DH, RT, R.B, B.M, and D.D, acknowledge the NEDO Grant for providing us with a wonderful opportunity of this international collaborative research project.

References

The list of the major papers from the project
References:


Symposium organized by project team